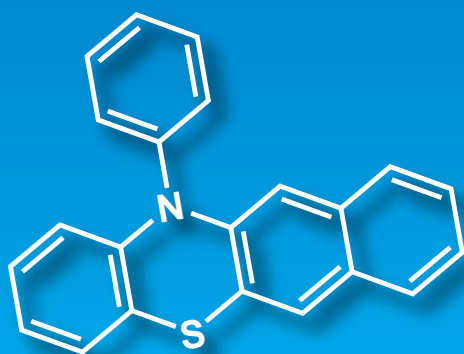
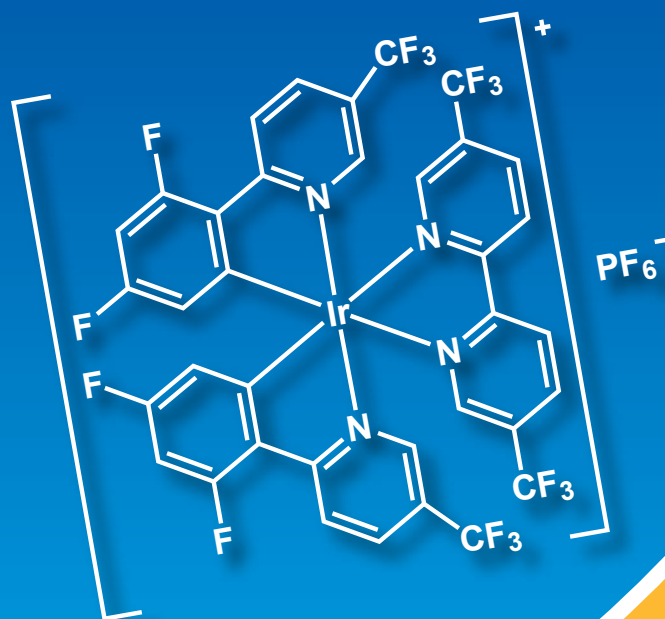
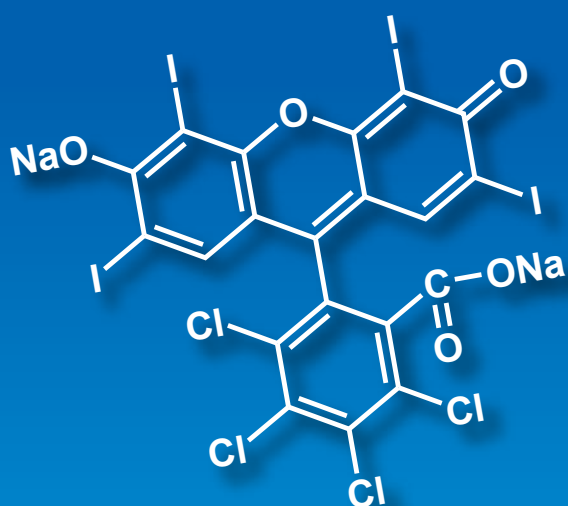


Organic Photoreaction Reagents



Photocatalysts

Reagents for Introducing Functional Group

Others

Organic Photoreaction Reagents

An organic photoreaction is a reaction in which the substrate is excited by light. Nowadays, photoreactions have established an important position in synthetic organic chemistry; however, the history of these reactions is surprisingly old, with reports indicating that light was relevant to organic reactions at the end of the 19th century.¹⁾ Photoreactions can be utilized in the construction of carbon skeletons and the conversion of functional groups that are difficult to achieve through thermal reactions. Conversely, thermal reactions can proceed in cases where photoreactions are challenging, demonstrating that the two reaction types are complementary. In addition, concerns about the depletion of carbon resources and the principles of green chemistry have renewed interest in photoreactions, which proceed simply by light irradiation. As a result, photoreactions have become a significant trend in reaction development. Furthermore, photoreactions have been widely used in the field of flow chemistry,²⁾ and novel coupling reactions in combination with transition metal catalysts have been reported.³⁾ Thus, it can be concluded that the potential of photoreactions continues to expand.

This brochure introduces photocatalysts used in organic synthesis and reagents that facilitate the introduction of functional groups through photoreactions. Reagents for materials development and life sciences involving light, such as photoinitiators and photoreactive crosslinkers, are not included. For information on these reagents, please refer to the PDF files available on our website.

Polymerization Initiators:

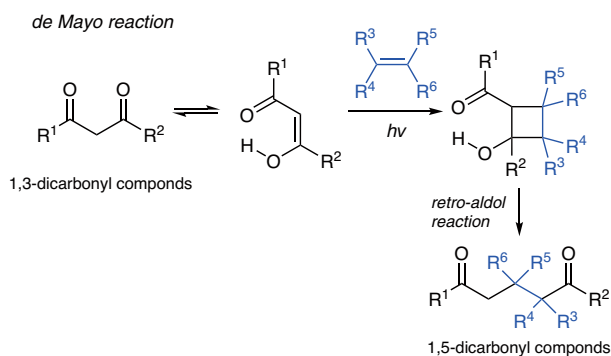
https://www.tcichemicals.com/assets/brochure-pdfs/Brochure_F2037_E.pdf

Photo-reactive Crosslinkers:

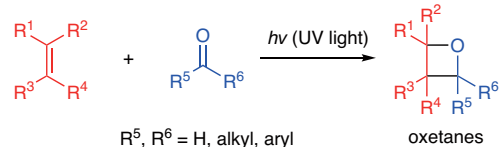
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● Conventional Organic Photoreactions

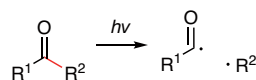
Organic photoreactions have been studied since the beginning of the 20th century, with de Mayo cycloaddition reactions,⁴⁾ Paternò-Büchi reactions,⁵⁾ and Norrish type I and II reactions⁶⁾ being known as well-known name reactions. The light sources for these reactions are typically sunlight or ultraviolet light.



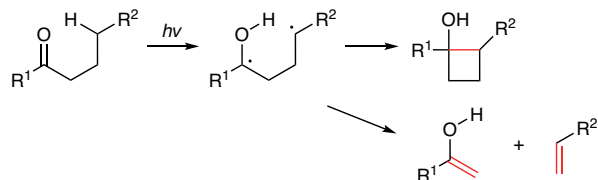
Paternò-Büchi reaction



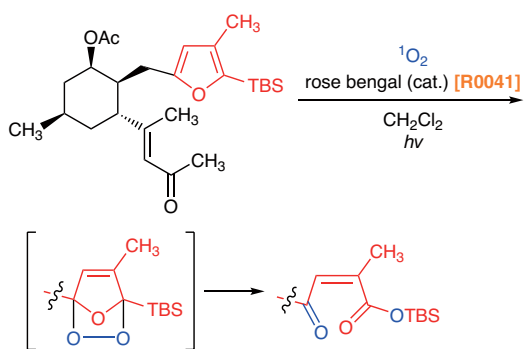
Norrish type I reaction



Norrish type II reaction

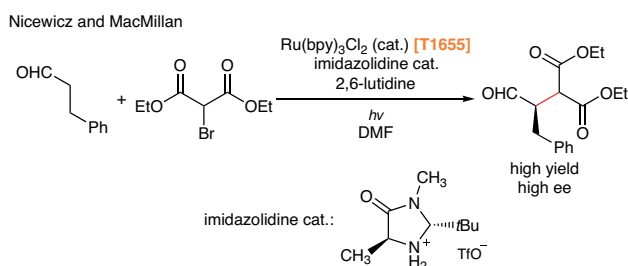


Photoreactions can be categorized into those in which the substrate is directly excited by light, and those in which a photosensitizer is first excited, transferring energy or electrons to the substrate. Photosensitizers include aromatic ring compounds such as benzophenone and phenanthrene, dyes, and the visible-light redox catalysts described below, which can also function as photosensitizers. The following reaction is an example where rose bengal is used as a photosensitizer to excite an oxygen molecule to singlet oxygen, followed by cycloaddition to a furan ring.⁷⁾

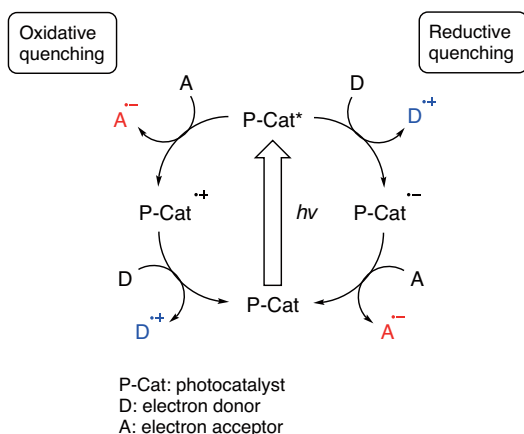


Visible-light Redox Reactions and Catalysts

It is no exaggeration to say that visible light photoredox reactions are one of the latest trends in organic reaction development. However, the history of these reactions is surprisingly long. A search for "photoredox" as a keyword in SciFinder[®], a chemical literature and reaction information search tool, reveals that the term first appeared in 1967.⁸⁾ Since then, the number of reports has increased rapidly, particularly from around 2010 onward, with more than 9200 reported cases by December 2023 and more than 1100 reports in 2023 alone. This growth can be attributed to a report on visible light redox reactions by McMillan in 2008⁹⁾ and the increased availability and widespread use of LED light sources in laboratories.



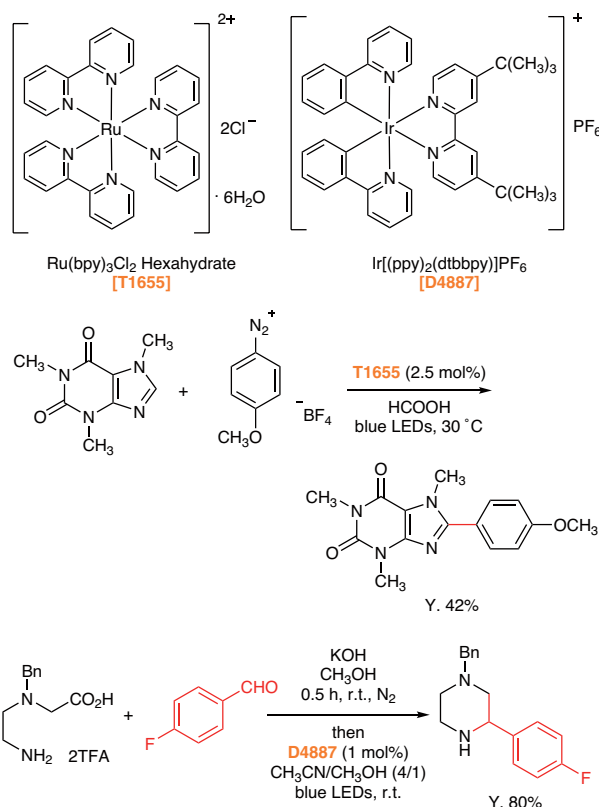
The reaction mechanism for photoredox reactions is illustrated in the figure below.¹⁰⁾ First, a photocatalyst (P-Cat) enters the triplet photoexcited state (P-Cat*) upon exposure to light. Then, following the cycle on the left (oxidative quenching), an electron acceptor (A) receives an electron from P-Cat*, producing A^- and P-Cat⁺. The catalytic cycle is then established when P-Cat⁺ accepts an electron from the electron donor (D), returning to P-Cat. Thus, in photoredox reactions, the catalytic cycle involves both oxidation and reduction.



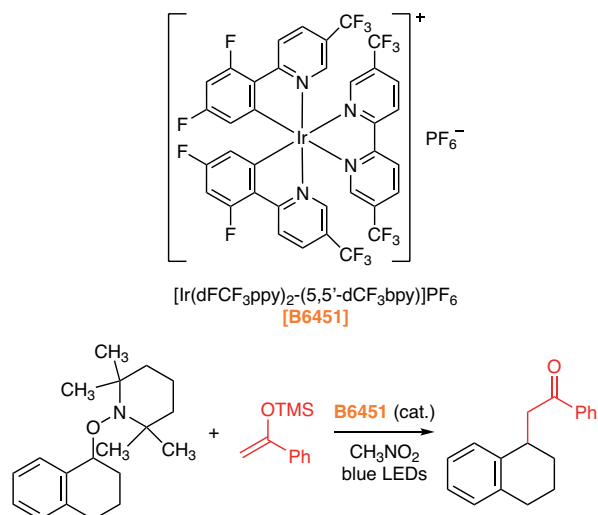
Here we introduce reaction examples related to our products, divided into metal complexes and organocatalysts. In addition, in the "Applications & Literature" tab of the product detail page for each redox catalyst, you will find application examples that have been operated by our staff through actual experiments. Please refer to these as well.

Organometallic Complexes

The central metals used primarily in visible light redox catalysts are iridium and ruthenium, and most of the complexes we handle are also made up of them.

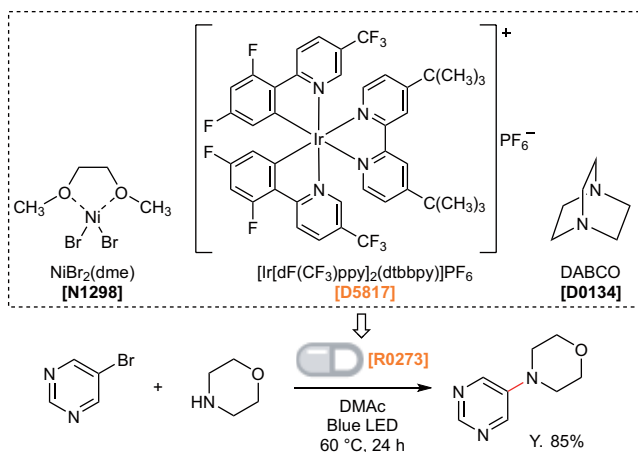


Metal complexes are characterized by the ability to adjust the redox potential through the substituents of the ligands. Among these, $[\text{Ir}(\text{dFCF}_3\text{ppy})_2-(5,5'\text{-dCF}_3\text{bpy})]\text{PF}_6$ (**B6451**) is known to exhibit more oxidative excited states than other iridium complexes.^{11,12)}



Since iridium and ruthenium are rare, reactions using more readily available metals are also being developed. Photoredox reactions using iron complexes are one example.¹³⁾

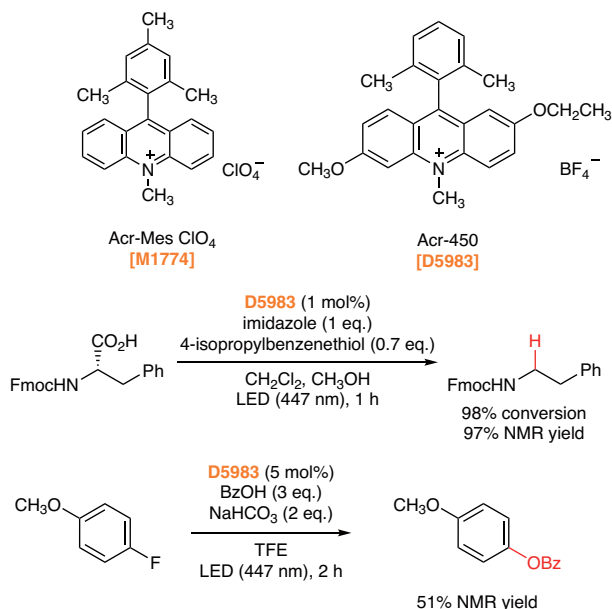
The visible light redox catalyst $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ [D5817] and a capsule reagent containing a predetermined amount of $\text{NiBr}_2(\text{dme})$ and DABCO can be used for metallo-photoredox C-N cross-coupling.¹⁴⁾ Since the capsules dissolve in the reaction mixture, the use of R0273 eliminates the need to weigh the base and catalyst.



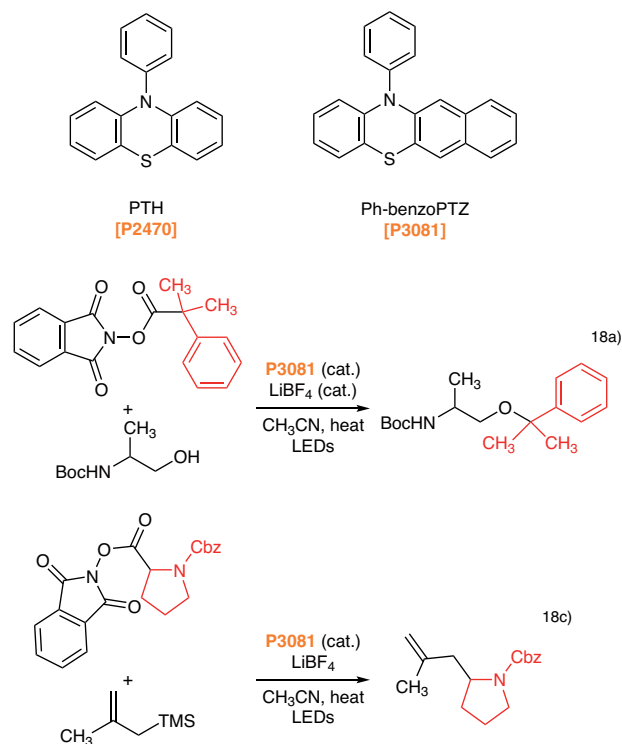
Organic Compounds

Although iridium and ruthenium complexes are effective as visible light redox catalysts, they have certain disadvantages. Iridium and ruthenium are rare and expensive metals, and residual heavy metal impurities are undesirable. Therefore, the use of organocatalysts has attracted attention. Fukuzumi *et al.* discovered that the triplet-excited state of Acr-Mes ClO_4 [M1774] has a high oxidation potential¹⁵⁾ and reported that it is effective as a visible light redox catalyst.

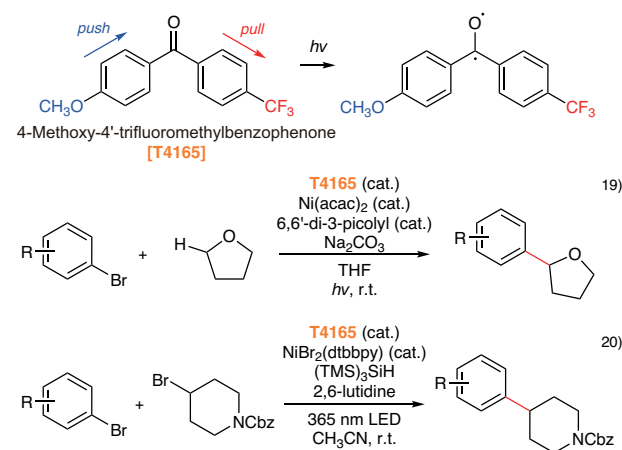
Acr-Mes ClO_4 subsequently become known as the Fukuzumi catalyst, and the development of new reactions and analogues increased. Acr-450 [D5983] is one such analogue and is known to have an absorption maximum at 450 nm, which is longer than that for Acr-Mes ClO_4 , and its reactivity is comparable to that of Acr-Mes ClO_4 .¹⁶⁾



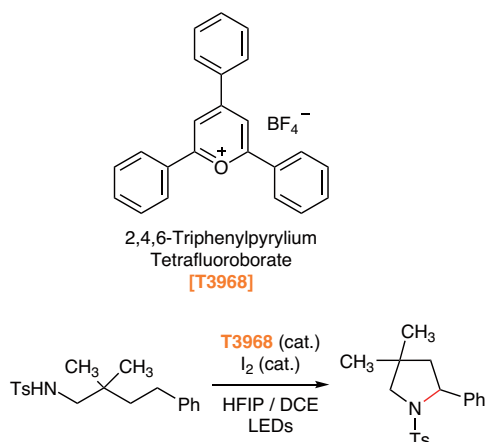
10-Phenylphenothiazine (= PTH) [P2470] and its derivatives have also been used as organocatalysts in visible light redox reactions.¹⁷⁾ One derivative, Ph-benzoPTZ [P3081], can be excited by blue light and catalyzes decarboxylative bond-formation reactions between sp^3 carbons and heteroatoms such as the esters of *N*-hydroxyphthalimides and alcohols and amines.^{18a,b)} Furthermore, carbon-carbon bond-formation reactions with organosilicon compounds have also been reported.^{18c)}



Benzophenone can be used as a photoredox catalyst, but excitation of benzophenone requires high-energy ultraviolet light, which can easily degrade the substrate. In contrast, 4-methoxy-4'-trifluoromethylbenzophenone [T4165] has a push-pull structure that increases the absorption wavelength. Consequently, T4165 can be used as a photoredox catalyst that operates under milder conditions, and its use as a catalyst for C(sp^2)-C(sp^3) cross-coupling has been reported.¹⁹⁾ T4165 has also been reported to catalyze the reductive cross-coupling reaction of aryl bromide with alkyl bromide.²⁰⁾

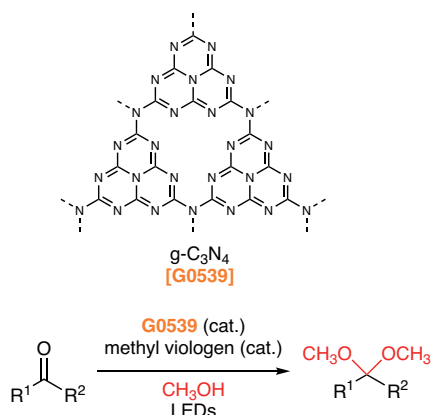


2,4,6-Triphenylpyrylium tetrafluoroborate acid **[T3968]** is an organic salt with highly oxidative excited states. **T3968** is used in the construction of heterocyclic rings, as shown in the reaction example below.²¹⁾

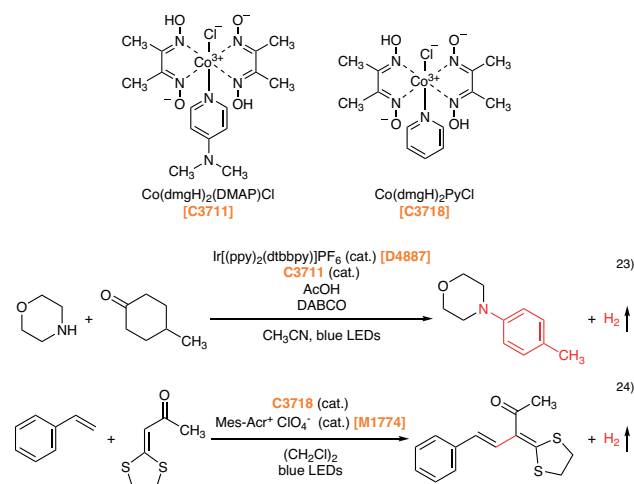


Inorganic Compounds

Graphitic carbon nitride (g-C₃N₄) **[G0539]** and its analogues are well known for their applications as photocatalysts as well as for the development of materials. While they are best known as catalysts for water splitting and organic removal, they have also been used as photoredox catalysts in organic synthesis.²²⁾



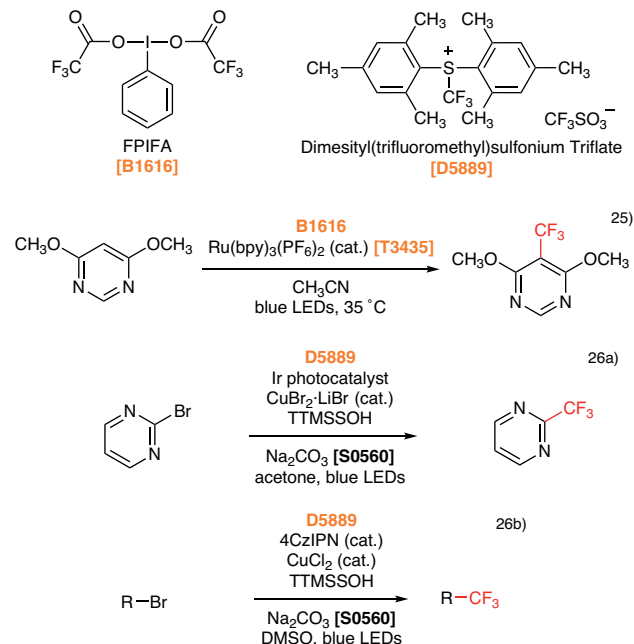
Some catalysts exhibit new reactivity when combined with photoredox catalysts. For example, the cobalt complexes Co(dmgH)₂(DMAP)Cl **[C3711]** and Co(dmgH)₂PyCl **[C3718]** are known to catalyze oxidant-free dehydrogenative coupling reactions²³⁾ and carbon-carbon bond formation²⁴⁾ in the presence of visible light redox catalysts. Other novel reactions in combination with metal complexes used in cross-coupling, such as palladium and nickel complexes, have also been actively investigated.



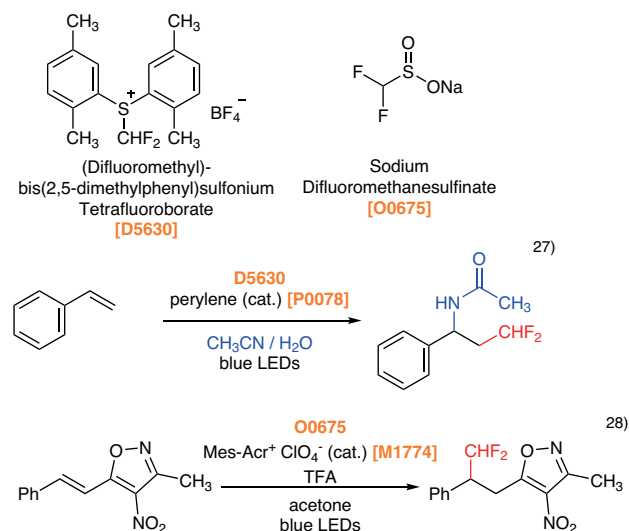
Photoreactive Functional Group Reagents

We offer not only catalysts for photoreactions, but also reagents that can introduce functional groups through photoreactions. Among these, fluorine-containing alkylating reagents are compatible with photoredox reactions, and a wide variety of reagents have been reported. Fluorine-containing functional groups are commonly found in bioactive substances and functional materials, and their efficient introduction during late-stage synthesis is highly desired in the development of new substances.

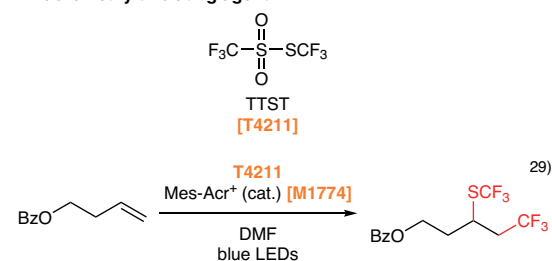
Trifluoromethylating agents



Difluoromethylating agents

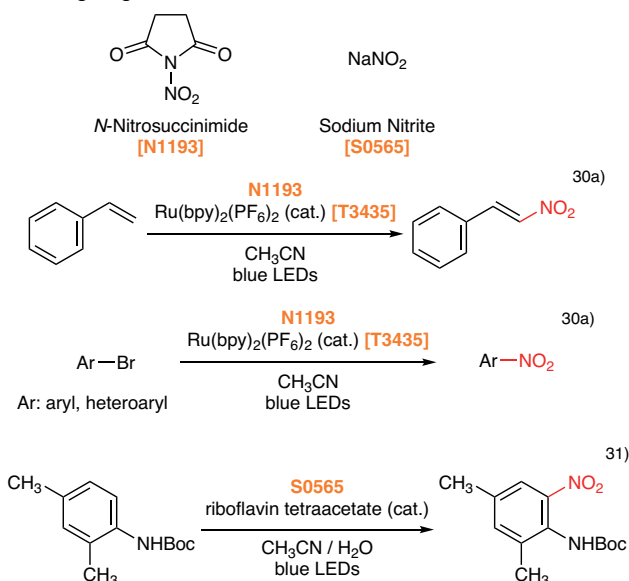


Trifluoromethylthiolating agent



In addition to fluoroalkylating agents, we also offer nitrating agents for introducing nitro groups under photoirradiation. *N*-Nitrosuccinimide **[N1193]** is useful not only for the introduction of nitro groups³⁰⁾ but also for the construction of oxazole rings through multicomponent reactions. The nitration of protected aniline derivatives by light using sodium nitrite **[S0565]** has also been reported.³¹⁾

Nitrating reagents



‡ SciFinder® is a registered trademark of the American Chemical Society.

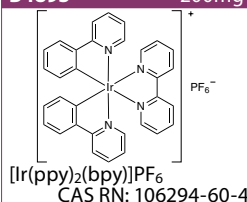
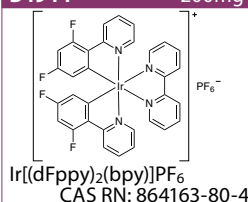
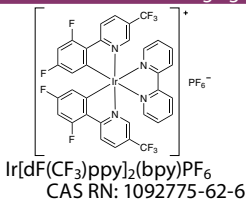
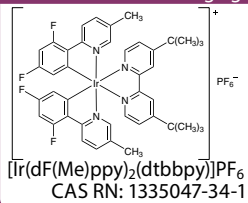
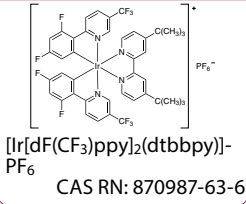
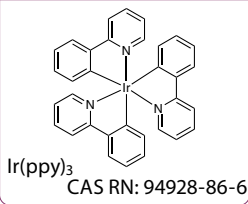
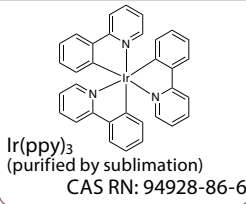
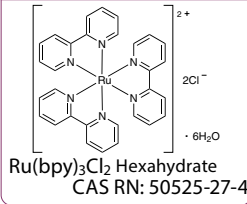
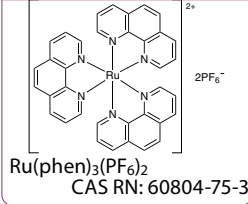
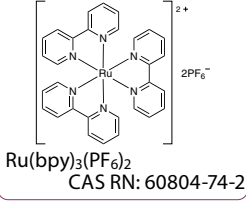
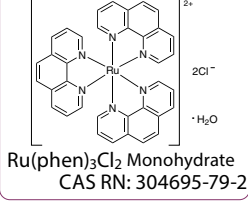
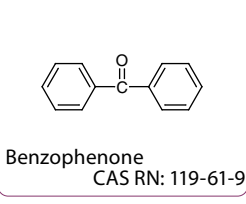
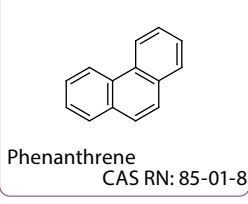
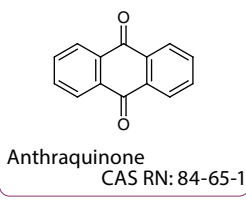
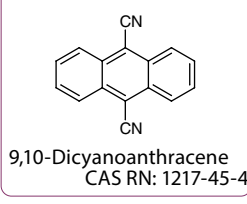
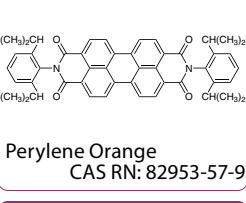
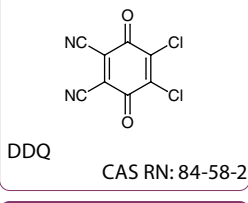
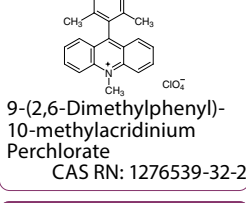
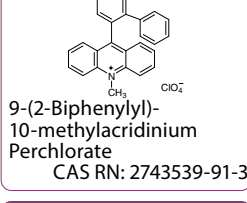
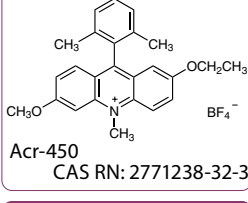
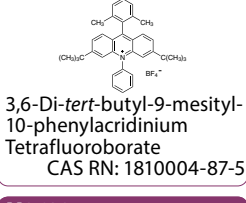
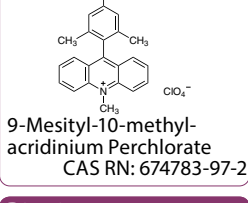
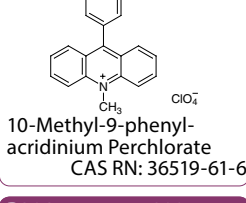
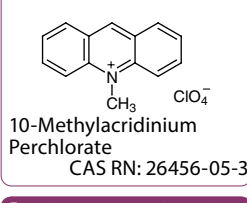
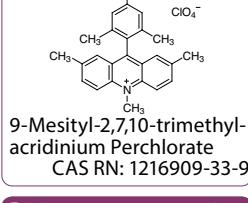
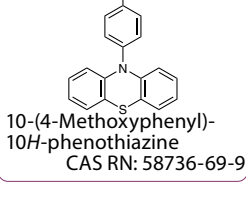
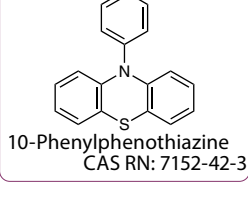
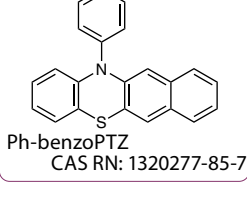
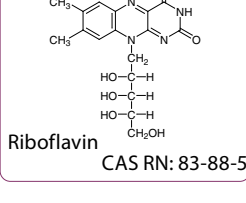
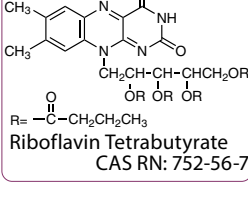
† Acr-450 is commercialized under the permission of Shionogi Pharma Co., Ltd. (WO2022107755).

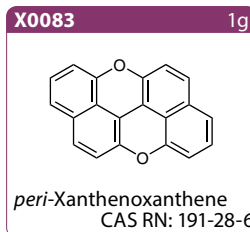
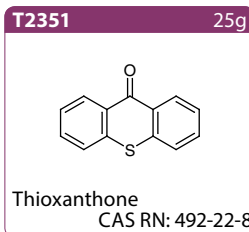
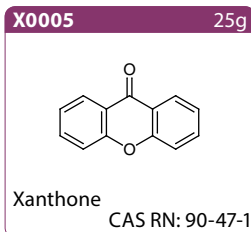
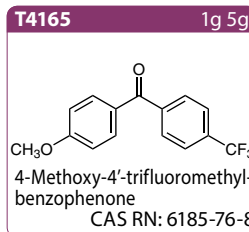
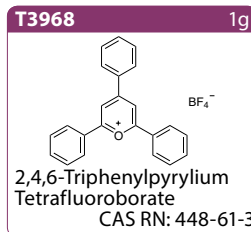
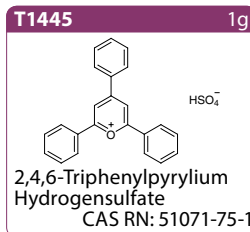
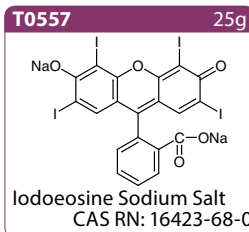
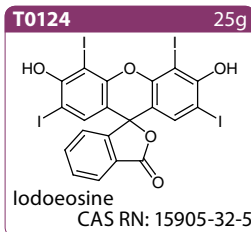
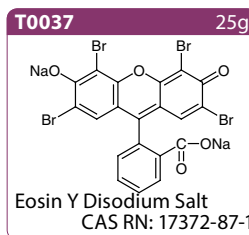
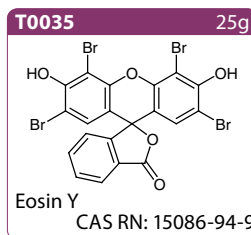
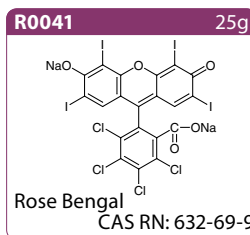
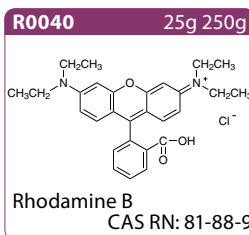
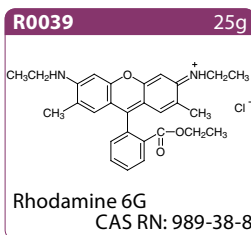
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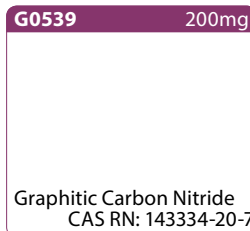
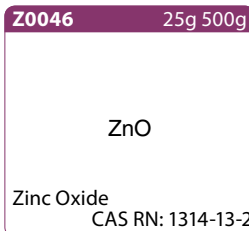
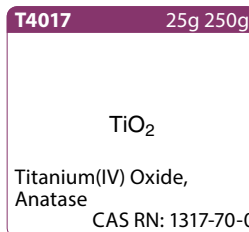
Photocatalysts

Organometallic Complexes

Photocatalysts		Organometallic Complexes		B4893 200mg  [Ir(ppy) ₂ (bpy)]PF ₆ CAS RN: 106294-60-4	B4944 200mg  Ir[(dFppy) ₂ (bpy)]PF ₆ CAS RN: 864163-80-4
				B6161 200mg 1g  Ir[dF(CF ₃)ppy] ₂ (bpy)PF ₆ CAS RN: 1092775-62-6	B6254 200mg 1g  [Ir(dF(Me)ppy) ₂ (dtbbpy)]PF ₆ CAS RN: 1335047-34-1
D5817 200mg 1g  [Ir(dF(CF ₃)ppy) ₂ (dtbbpy)]-PF ₆ CAS RN: 870987-63-6	T3716 200mg 1g  Ir(ppy) ₃ CAS RN: 94928-86-6	T1946 200mg  Ir(ppy) ₃ (purified by sublimation) CAS RN: 94928-86-6	T1655 1g 5g  Ru(bpy) ₃ Cl ₂ Hexahydrate CAS RN: 50525-27-4	T3208 200mg 1g  Ru(phen) ₃ (PF ₆) ₂ CAS RN: 60804-75-3	
T3435 1g  Ru(bpy) ₃ (PF ₆) ₂ CAS RN: 60804-74-2	T3902 1g  Ru(phen) ₃ Cl ₂ Monohydrate CAS RN: 304695-79-2	C0449 100mg 1g Vitamin B ₁₂ CAS RN: 68-19-9	R0273 10each Reagents for Metallophotoredox Cross-Coupling Reactions [NiBr ₂ (dme), [Ir(dF(CF ₃)ppy) ₂ (dtbbpy)]PF ₆ , DABCO] (HPMC encapsulated)	Organocatalysts	
B0083 25g 500g  Benzophenone CAS RN: 119-61-9	P0079 25g 500g  Phenanthrene CAS RN: 85-01-8	A0502 25g 500g  Anthraquinone CAS RN: 84-65-1	D1656 1g 5g  9,10-Dicyanoanthracene CAS RN: 1217-45-4		
B4268 1g 5g  Perylene Orange CAS RN: 82953-57-9	D1070 25g 250g  DDQ CAS RN: 84-58-2	D3429 1g  9-(2,6-Dimethylphenyl)-10-methylacridinium Perchlorate CAS RN: 1276539-32-2	B2897 1g 5g  9-(2-Biphenyl)-10-methylacridinium Perchlorate CAS RN: 2743539-91-3	D5983 200mg 1g  Acr-450 CAS RN: 2771238-32-3	
D6218 100mg  3,6-Di- <i>tert</i> -butyl-9-mesityl-10-phenylacridinium Tetrafluoroborate CAS RN: 1810004-87-5	M1774 1g 5g  9-Mesityl-10-methylacridinium Perchlorate CAS RN: 674783-97-2	M1775 1g 5g  10-Methyl-9-phenylacridinium Perchlorate CAS RN: 36519-61-6	M1787 250mg 1g  10-Methylacridinium Perchlorate CAS RN: 26456-05-3	M2072 1g  9-Mesityl-2,7,10-trimethylacridinium Perchlorate CAS RN: 1216909-33-9	
M3639 1g 5g  10-(4-Methoxyphenyl)-10H-phenothiazine CAS RN: 58736-69-9	P2470 1g 5g  10-Phenylphenothiazine CAS RN: 7152-42-3	P3081 200mg 1g  Ph-benzoPTZ CAS RN: 1320277-85-7	R0020 25g 100g 500g  Riboflavin CAS RN: 83-88-5	R0055 5g 25g  Riboflavin Tetrabutryate CAS RN: 752-56-7	

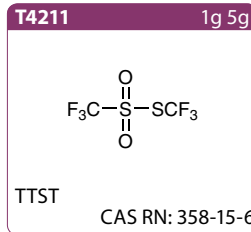
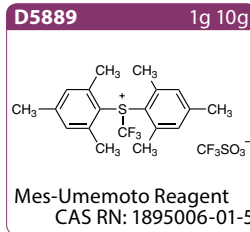
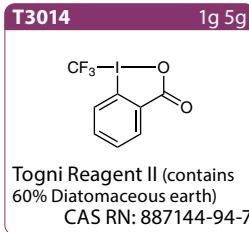
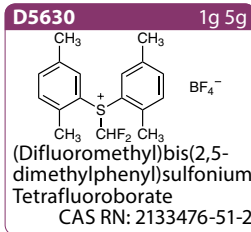
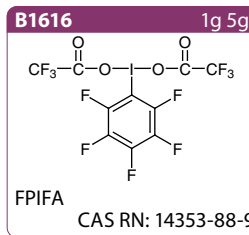
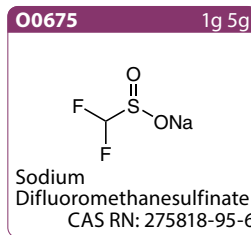


**Inorganic
Catalysts**

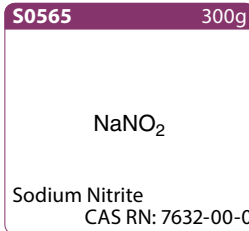
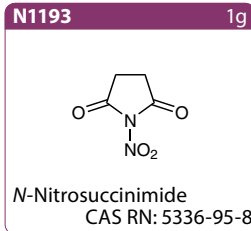


**Reagents for
Introducing Functional
Group**

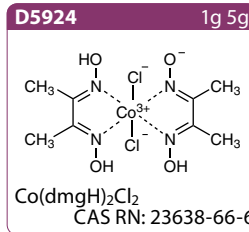
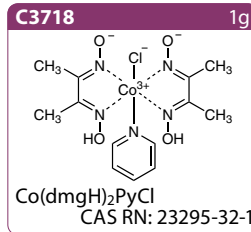
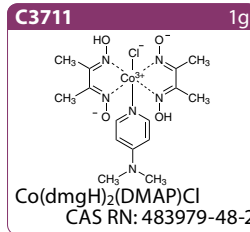
**Fluoroalkylating
Reagents**



**Nitrating
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Others



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